Screening of Selected Pesticides for Possible Future Consideration as Candidates for Biomonitoring in California

Glufosinate Ammonium, Glyphosate, Imidacloprid, Propanil

Materials for August 14, 2013 Meeting of Scientific Guidance Panel (SGP) for Biomonitoring California¹
Agenda Item: Chemical Selection Planning

The purpose of this document is to provide background information for the Scientific Guidance Panel's (SGP's) discussion of four pesticides for possible future consideration as candidates for biomonitoring in California. The four pesticides are glufosinate ammonium, glyphosate, imidacloprid, and propanil.

The SGP, the public and State staff have requested that the Program screen high use pesticides for possible biomonitoring in California. The four pesticides in the current screening document are all on the California Department of Pesticide Regulation's (DPR) list of top 100 pesticides used in California in 2011. The pesticides were selected for screening because they are either high on the top 100 list (glyphosate, propanil), have shown recent increases in use (glufosinate), or have potential for residential/household exposure (glyphosate, imidacloprid).

This document includes a brief summary of information located so far on:

- Chemical identity and structure
- Type of pesticide and uses
- Volume applied in California
- Other data relevant to exposure
- Physical chemical properties
- Predicted bioaccumulation and persistence
- Some toxicity endpoints
- Pharmacokinetic factors
- Human biomonitoring

A comprehensive literature search was not conducted. Secondary sources and predictive tools were used for some of the information.

At the August 14 meeting, the Panel will recommend what next steps, if any, should occur. The SGP could recommend that the Program develop a document or documents to support consideration of one or more of the pesticides in this screen as potential designated chemicals. Another option would be for the SGP to recommend further screening of one or more of these pesticides. The Panel could also recommend no further action on any of these.

¹ California Environmental Contaminant Biomonitoring Program, codified at Health and Safety Code section 105440 et seq.

Chemical Name [CASRN]	Struc	ture	Type of pesticide and uses
Glufosinate ammonium [77182-82-2]	O 	O- NH ₄ ⁺	Herbicide; crop dessicant Used on conventional and genetically modified crops Example crops: Corn, canola, soybeans, tree nuts (like almonds and walnuts), grapes, potatoes Other: Rights-of-way; spot treatments on recreational fields and residential lawns
Glyphosate [1071-83-6] (Major salts: glyphosate isopropylamine salt [38641- 94-0]; glyphosate potassium salt [39600-42-5])	НО	О Р ОН	Herbicide; plant growth regulator Used on conventional and genetically modified crops Example crops: Corn (including forage/fodder), soybeans, cotton, tree nuts (like almonds), grapes, oranges Other: Rights-of-way, landscape maintenance, residential garden maintenance

Chemical Name [CASRN]	Structure	Type of pesticide and uses
Imidacloprid [138261-41-3]	CI N N N N N N N N N N N N N N N N N N N	Insecticide Example crops: grapes, lettuce, citrus (like oranges), tomato (processing), potatoes, broccoli Other: structural pest control, landscape maintenance, golf courses, pet pesticide, lawn and ornamental plant maintenance, invasive species control
Propanil [709-98-8]	NH CI	Herbicide Food crop: rice

Screening of Selected Pesticides

Chemical name	Pounds applied in CA ²	2011 Pounds sold in CA ³	Other data relevant to exposure	
Glufosinate ammonium	2007: 131,634 1,299,405 2008: 344,200 2009: 461,577 2010: 657,883		Current residue monitoring data not located. From experimental studies in Europe, residues of up to 0.5 ppm detected in potatoes treated with glufosinate as a dessicant. Detected infrequently in U.S. monitoring of surface water and	
	2011: 740,327		groundwater; not detected in California.	
Glyphosate (all forms)	2007: 7,236,785 2008: 6,915,054 2009: 7,145,493 2010: 8,676,349 2011: 10,745,583	21,016,705	Residues of glyphosate detected in 271/300 samples of U.S. soybeans (range, 0.26-18.5 ppm).	
			Residues of degradate/metabolite AMPA (aminomethylphosphonic acid) detected in 287/300 samples of U.S. soybeans (range 0.26-20 ppm)	
			Glyphosate and AMPA detected in some U.S. surface waters, including in California, and in some U.S. groundwater samples.	
			Glyphosate detected in house dust in Iowa (farm and non-farm homes).	
Imidacloprid	2007: 334,623 2008: 159,407 2009: 196,048	1,502,469	Residues reported in CA produce monitoring program ranged from 0.012 -0.616 ppm.	
	2009: 196,048 2010: 266,327 2011: 290,291		Wipe tests showed transfer from dogs' coats continued through four weeks after spot-on treatment.	

² California Department of Pesticide Regulation (CDPR): http://www.cdpr.ca.gov/docs/pur/purmain.htm
³ CDPR: http://www.cdpr.ca.gov/docs/mill/pdsd2011.pdf
Includes sales for agricultural, commercial and consumer uses.

Screening of Selected Pesticides

Chemical name	Pounds applied in CA ²	2011 Pounds sold in CA ³	Other data relevant to exposure
Propanil	2007: 1,801,607 2008: 1,724,068 2009: 1,904,607 2010: 1,993,021 2011: 2,221,773	2,743,410	Residues of propanil or 3,4-DCA ⁴ on tested rice samples ranged from 0.03 ppm to 8.7 ppm (US EPA). No residues were reported on polished rice. 1/435 detections in rice samples (USDA). Propanil or 3,4-DCA detected in ambient air and in surface and groundwater in some CA counties.

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⁴ 3,4-DCA (3,4-dichloroaniline) is the environmental degradate and plant metabolite of propanil.

5	Molecular	Log	Vapor	Water	7	Half-life (days) ⁸			
Chemical ⁵	weight (g/mol)	Log K _{ow}	pressure (mm Hg) ⁶	solubility (mg/L) ⁶	BCF ⁷	Water	Soil	Marine sediment	Ambient air
Glufosinate	181.13	-3.9	1.12E-10	1.0E06 ^{(SRC)9} 1.0E04 ^(PBT)	3.2	15	30	140	0.39
3-MPPA ¹⁰ (3-Methylphosphinicopropionic acid; MPP)	152.09	-0.8	1.3E-05	1.0E04	3.2	15	30	140	5.8
Glyphosate	169.07	-5.4	1.6E-08	1.0E06	3.2	15	30	140	0.2
AMPA ¹⁰ (Aminomethylphosphonic acid)	111.04	-2.1	5.8E-05	1.0E04	3.2	15	30	140	0.54
Propanil	218.08	3.07	9.1E-07	1.5E02	49	60	120	540	4.2
3,4-DCA ¹⁰ (3,4-Dichloroaniline)	162.02	2.69	6.3E-03	9.2E01	28	38	75	340	0.71
Imidacloprid	255.67	0.57	1.7E-06	6.1E02	3.2	60	120	540	0.1

Selevant chemical species listed

Nalues from PBT Profiler (http://www.pbtprofiler.net). Experimental values are shown in bold and estimated values are shown in plain text; all values at 25°C.

BCF = Bioconcentration factor. Values were estimated using PBT Profiler (http://www.pbtprofiler.net).

Half-life values were estimated using PBT Profiler (http://www.pbtprofiler.net). Orange indicates persistent (P) and red indicates very persistent according to U.S. EPA criteria.

⁹ From SRC Inc. Physprop database (http://www.srcinc.com/what-we-do/databaseforms.aspx?id=386)

¹⁰ Metabolite and/or environmental degradate

Chemical ¹¹	Some toxicity endpoints ¹²	Pharmacokinetic factors (based on studies in laboratory animals)	Human biomonitoring
Glufosinate	Reproductive and developmental toxicity Neurotoxicity	5-10% oral absorption Rapid excretion, primarily as parent compound in feces	Glufosinate and 3-MPPA reported in serum (Quebec, Canada). Refer to Aris and Leblanc (2011) and Blacker et al. (2011) for more details.
Glyphosate	Developmental toxicity Indication of endocrine activity (decrease in aromatase activity)	30-36% oral absorption; poor dermal absorption Rapid excretion, predominantly as parent compound. Greater excretion in feces.	Glyphosate detected in urine: Farm (Iowa, S. Carolina, Minnesota) and non-farm families (Iowa) Adults from 18 European countries (unpublished study); also detected AMPA
Imidacloprid	Developmental neurotoxicity	>90% oral absorption Rapid excretion, primarily via urine.	No biomonitoring studies located
Propanil	Immunotoxicity	Rapid oral absorption of 3,4-DCA, plant metabolite and environmental degradation product of propanil. Rapid excretion, predominantly in urine	3,4-DCA detected in urine. 13 Adults, rural central Italy Farmers, Italy 3,4-DCA-hemoglobin adducts detected in blood of 2 agricultural worker volunteers

Many studies tested commercial formulations (including an adjuvant for example) or technical grade chemicals.

This column provides information located so far on some toxicity endpoints, including from secondary sources. If any of these chemicals are chosen for further consideration, the known or suspected health effects will be reviewed and described in more detail.

13 3,4-DCA is also a metabolite of diuron and linuron.

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